



Ceria based solid catalysts for Fenton's depuration of phenolic wastewaters, biodegradability enhancement and toxicity removal

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ABSTRACT

The depuration of a simulated wastewater comprising six phenolic acids usually present in Olive Mill Wastewaters was studied by heterogeneous Fenton's technology. Several process parameters have been evaluated including catalyst load, hydrogen peroxide concentration and pH revealing that laboratorial Fe-Ce-O catalyst was the most active formulation with a molar ratio between Fe and Ce of 70/30. On the assessment of process efficiency, the optimum values achieved led to the selection of target values: 1.0 g L^{-1} of Fe-Ce-O 70/30, $[\text{H}_2\text{O}_2] = 244 \text{ mM}$ and pH 3 being removed the total phenolic content and 57% mineralization after 120 min of reaction time. Cutting edge environmental classification parameters such as biodegradability enhancement and toxicity reduction were considerably improved with heterogeneous Fenton's process which enables its successful application as pre-treatment before a biological methodology. Catalytic characterization was deployed structural and morphologically whereas catalytic stability in terms of metal leaching and carbonaceous adsorption showed that used catalysts kept the oxidation efficiency in comparison with fresh ones. Finally, stability during several reuses was evaluated through the implementation of feed-batch trials reinforcing the benefits of ceria based catalysts.

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1. Introduction

Mankind, on the race for new products to sustain the actual needs has been unsustainably using the natural resources and producing large amount of wastes which seriously damage our ecosystems. Water streams depletion and contamination appears as one special concern connected with the irresponsible discharge of liquid effluents to the natural courses. The traditional treatment methodologies are generally based on biological processes due to their simplicity and low operational costs. Nevertheless, these technologies are limited to non-toxic and highly biodegradable wastewaters. Furthermore, they are quite sensitive to changes on effluent characteristics not being, hence, adequate to seasonal residues such as the Olive Mill Wastewaters (OMW) which are only produced along a few months of the year and rich in highly toxic organic loads of phenolic compounds [1].

The development and application of several Advanced Oxidation Processes (AOPs) to the depuration of OMW concentrated significant research in the field of environmental reaction engineering during the last decades [2]. Fenton's process is an interesting solution since it allows high depuration levels at room tempera-

ture and pressure conditions using innocuous and easy to handle reactants. The main drawback is related with the large amount of iron required (between 50 and 80 mg L^{-1}) [3] to have an efficient treatment that is much higher than the one legally permitted for effluents discharge ($<2 \text{ mg L}^{-1}$). It is then necessary to promote the metal separation from the liquid phase which leads to the formation of large quantities of ferrous sludge, which demand in turn, a waste final management. Within this context, the enhancement of the hydrogen peroxide decomposition through a solid catalyst rather than homogenous iron seems to be a promising alternative, so that in the last decades some attempts were made to develop heterogeneous catalysts to be integrated in the Fenton's process. The use of several ligands to complex iron was investigated [4] and iron incorporation into porous supports has been studied as well. Among those solids it should be referred the application of Al-pillared clays [5], zeolites [6,7], clay [8,9], modified polyacrylonitrile (PAN) [10], activated carbon [11,12] and carbon aerogels [13].

In this work and for the purpose of catalytic activity screening studies, the heterogeneous Fenton's degradation of a mixture of six phenolic acids usually present in the real OMW was investigated with several composite commercial and laboratorial catalysts. After a catalyst screening, the process efficiency was evaluated on the effect of the main variables: pH, catalyst and hydrogen peroxide concentration.

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2. Experimental

2.1. Catalyst preparation and characterization

The commercial catalyst N-150 (Fe-Mn-O) was provided by Süd-Chemie AG (Munich, Germany). The laboratorial catalysts Fe-Mn-O (70/30), Fe-Ce-O (80/20), (70/30), (50/50), (30/70), Fe-O and Ce-O were prepared by co-precipitation. The respective metals nitrate salts were used as precursors, dissolved in 100 mL according to the molar proportion defined, so that the total salt dosage was not higher than 15 g [14]. 200 mL of sodium hydroxide (3 M) were added to promote precipitation and the solid obtained was filtrated and washed with distilled water. The filtrate was dried overnight at 105 °C and calcination of the crushed solid was performed at 300 °C during 3 h.

The selected catalyst was analyzed before and after utilization by Scanning Electron Microscopy (SEM) with a JEOL JSM-5310 and by X-ray powder diffraction (XRD) with a Philips PW 3040/00 X'Pert analyzer. The catalyst Brunauer–Emmet–Teller surface area (S_{BET}) was determined using nitrogen (−196 °C) with an accelerated surface area and porosimetry analyzer (ASAP 2000, Micromeritics). Mercury porosimetry (Poresizer 9320, Micromeritics) was used for porosimetry and pore size distribution assessment. The catalysts content in C, H, N and O was determined by Elemental analysis with a Fisons Instruments EA 1108 CHNS-O.

2.2. Oxidation procedure

Fenton's oxidation was carried out in a stirred glass reactor using 300 mL of wastewater. pH was followed up and kept constant during the experiments by adding either H_2SO_4 or NaOH when necessary. After the addition of the catalyst, the reaction begins when H_2O_2 is introduced in the reactor. Along the process, samples were withdrawn and immediately filtrated (filter with 0.45 μm pore diameter) to remove the catalyst. NaOH was added to quench the remaining H_2O_2 since it interferes with some of the analytical techniques. In fact, at pH values higher than 4, H_2O_2 quickly decomposes into molecular oxygen [9,15]. The addition of NaOH can promote leached metals precipitation as hydroxides that may remove organic compounds by adsorption. Nevertheless, no solids formation was detected in the withdrawn samples and, therefore, that effect was neglected.

Most of the experiments were performed at room temperature ($T \approx 20^\circ\text{C}$); nevertheless, when the effect of that parameter was addressed, the runs at higher values of temperature were carried out in an oven.

2.3. Analytical techniques and synthetic wastewater preparation

The liquid samples were analyzed for Total Organic Carbon (TOC) using a Shimadzu 5000 Analyser equipped with an auto-sampler (ASI – 5000A) whereas the Total Phenolic Content (TPH) was measured colourimetrically by the Folin–Ciocalteu procedure [16,17]. 20 μL of sample were introduced in a 2 mL cuvette and diluted with 1.58 mL of deionised water. 100 μL of the Folin–Ciocalteu reagent were added and after 3–6 min 300 μL of a saturated sodium carbonate solution were introduced. After 2 h in the dark, the absorbance at 765 nm was measured with a T60 PG Instruments spectrophotometer against a blank solution containing 20 μL of deionised water instead of the sample. Since the calibration curve was obtained using standard solutions of gallic acid TPH is given as equivalent mg L^{-1} of gallic acid. Chemical Oxygen Demand (COD) was determined according to the Standard Method 5220D [18] using a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer. The Biochemical Oxygen Demand after 5 days (BOD_5) was measured by the method proposed in the

Standard Methods being the inoculums obtained from garden soil [19]. High Performance Liquid Chromatography (HPLC) was used aiming to detect some of the reaction intermediates namely malonic, formic, acetic, oxalic and benzoic acids as well as phenol since some of these were previously identified as by-products of the catalytic ozonation of this phenolic mixture. The samples were injected via autosampler (Knauer Smartline Autosampler 3800), using a mobile phase (20% of methanol in water slightly acidified) pumped by a Knauer WellChrom K-1001 pump at a flow rate of 1 mL/min through an Eurokat H column at 85 °C being the detection performed at 210 nm [19].

To infer about the samples impact over the ecosystems if discharged to the natural water courses, their toxicity was evaluated by the marine bacteria *Vibrio fischeri* light inhibition after 15 min of incubation on the presence of the potential toxic effluent. This procedure was carried out with the commercial analyzer LUMISTox (Dr. Lange, Germany) which operates according to the standard DIN/EN/ISO 11348. Hence, the wastewater effective concentration that causes the inhibition of 20% (EC_{20}) and 50% (EC_{50}) of the bacteria consortium was obtained. Biodegradability and toxicity were also measured using respirometric techniques in a Liquid Static-Static (LSS) respirometer. For biodegradability measurement the Oxygen Uptake Rate (OUR) on the presence of a totally biodegradable compound ($\text{OUR}_{\text{Acetic Acid1}}$) of activated sludges (3000–4000 mg/L of Volatile Suspended Solids, obtained from a winery wastewater treatment plant) was compared with the OUR when the sludge was fed with the wastewater sample ($\text{OUR}_{\text{Sample}}$) according to Eq. (1). The toxicity was obtained by comparing the bacteria OUR with acetic acid before ($\text{OUR}_{\text{Acetic Acid1}}$) and after ($\text{OUR}_{\text{Acetic Acid2}}$) being in contact with the potentially toxic sample as shown on Eq. (2).

$$\% \text{Biodegradability} = \left(\frac{\text{OUR}_{\text{Sample}}}{\text{OUR}_{\text{Acetic Acid1}}} \right) \times 100 \quad (1)$$

$$\% \text{Toxicity} = \left(\frac{\text{OUR}_{\text{Acetic Acid1}} - \text{OUR}_{\text{Acetic Acid2}}}{\text{OUR}_{\text{Acetic Acid1}}} \right) \times 100 \quad (2)$$

Each sample was analyzed in triplicate to minimize the experimental error. The deviations between runs were always lower than 2%, 10%, 5%, 10%, 2% and 8% for TOC, TPh, COD, BOD_5 , LUMISTox and respirometry measurements, respectively. pH was monitored with a Crison micro pH 2000. Atomic absorption was used to quantify the leaching of iron to the liquid phase and the analysis was performed in a spectrometer Perkin-Elmer 3300.

The simulated effluent was prepared with 100 mg L^{-1} of each of the following six phenolic acids: Syringic acid (4-hydroxy-3,5-dimethoxybenzoic), vanillic acid (4-hydroxy-3-methoxybenzoic), 3,4,5-trimethoxybenzoic acid, veratric acid (3,4-dimethoxybenzoic), protocatechuic acid (3,4-dihydroxybenzoic) and 4-hydroxybenzoic acid (Sigma–Aldrich) usually present in the real OMW. The resulting effluent presented a TPh = 350 $\text{mg}_{\text{gallic acid}} \text{ L}^{-1}$, a TOC = 370 $\text{mg}_\text{C} \text{ L}^{-1}$ and 970 $\text{mg O}_2 \text{ L}^{-1}$ of COD. The toxicological tests (LUMISTox) revealed the high toxicity of this wastewater. In fact, 20% of the bacteria were inhibited through the contact with a solution involving only 4.5% of the wastewater while 32.2% of the effluent provoked the inhibition of 50% of *V. fischeri*. Barely 2% of biodegradability was determined respirometrically and a low BOD_5/COD of 0.3 allows concluding that this wastewater can be considered as partially biodegradable according to Sarria et al. [20] since it is below the threshold of 0.4 above which is commonly accepted that a stream is easily biodegradable [20–23]. Moreover, the contact with the effluent had negative impact over the activated sludge due to its toxicity which was inferred to be 67% by respirometry.

3. Results and discussion

3.1. Preliminary results

In order to establish the operational conditions leading to negligible mass transfer resistances preliminary experiments were performed to ensure the operation in chemical regime conditions. This fact has been accomplished with several oxidation runs featuring different values of stirring speed and catalyst particle sizes. Accordingly, particles with diameters in the range 250–500 μm stirred at 600 rpm assured negligible intraparticle and film mass transfer limitations. Before analyzing the catalytic activity under several experimental conditions, the effect of hydrogen peroxide capacity on wastewater decomposition without the addition of a heterogeneous catalyst was checked out leading to negligible COD removal that was lower than 2% after 120 min of reaction time. The catalysts adsorption capacity was also appraised in the absence of hydrogen peroxide and once again low organic matter was eliminated after 120 min measured as COD (<2% for N-150 and <7% for Fe-Mn-O (70/30) and Fe-Ce-O (70/30)).

3.2. Screening of catalysts

Iron is well known by its role within Fenton's chemistry due to the high capacity to promote hydrogen peroxide decomposition into highly reactive free radicals. Among the different commercial catalysts tested in our research group on the scope of other wastewater chemical oxidation technologies such as Catalytic Wet Oxidation [24] and Catalytic Ozonation [19], N-150 (Fe-Mn-O 60%/30%) integrates this element and was, therefore, selected for Fenton's tests. To compare this commercial Fe-Mn catalyst with a laboratorial one, a Fe-Mn-O (70/30) was prepared by co-precipitation. Given that the lanthanide Ceria-based catalysts are generally considered as promising formulations in the majority of the catalytic treatments [25–28] the Fe-Ce-O (70/30) was also investigated in the realm of heterogeneous Fenton's process.

The efficiency of the three selected catalysts over the heterogeneous Fenton's oxidation of the simulated wastewater was tested using a catalyst load of 1.0 g L^{-1} , $[\text{H}_2\text{O}_2] = 244 \text{ mM}$, pH 3 and room temperature. These experimental conditions were selected according to some literature results [9,10,29], moreover the hydrogen peroxide corresponds to four times the stoichiometric amount theoretically necessary to totally degrade the initial pollutants (61 mM). Fig. 1 represents the trends of TPh (a) and TOC (b) depletion. According to this figure, one can observe that all the catalytic systems under study are quite efficient on TPh degradation, with high initial removal rates and decompositions higher than 50% after 120 min of reaction time. N-150 catalyst shows to be the less active catalyst presenting the lowest efficiency with about 57% of TPh removed at the end of the experiment, whereas, considering the laboratorial ones, a similar degradation profile was identified for the first 20 min of Fenton's oxidation achieving 75% of TPh depletion. From this time onwards, while the catalytic system referred as Fe-Mn-O (70/30) reaches a plateau, where no further significant removal occurs, probably due to the formation of refractory intermediate compounds with phenolic character that we unsuccessfully tried to identify by HPLC (namely malonic, formic, acetic, oxalic and benzoic acids as well as phenol), the catalyst Fe-Ce-O (70/30) exhibited the best results on TPh abatement with total degradation after 120 min of oxidation treatment. The higher catalytic activity of Fe-Ce-O (70/30) was also confirmed in what concerns the wastewater mineralization during the oxidation run as shown in Fig. 1(b), where for 2 h of reaction time 35%, 45% and 57% of TOC removal was obtained for N-150, Fe-Mn-O (70/30) and Fe-Ce-O (70/30), respectively. Both TPh and TOC profiles suggest the typical two stages of Fenton's process comprising a very fast ini-

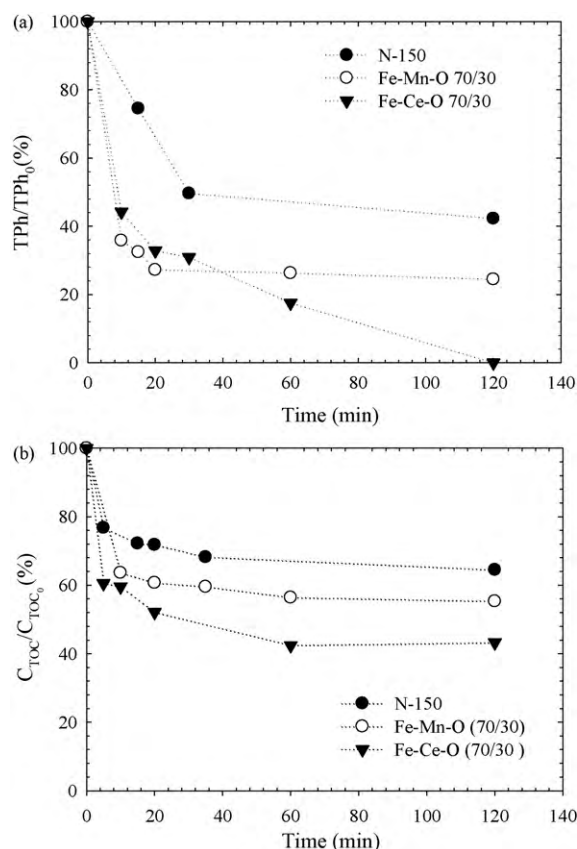


Fig. 1. (a) Normalized TPh and (b) TOC evolution during heterogeneous Fenton's process over the commercial and the laboratorial catalysts studied. (1.0 g L^{-1} of catalyst, $[\text{H}_2\text{O}_2] = 244 \text{ mM}$ and pH 3.)

tial decay followed by a slower degradation rate which is related with the Fe redox cycle [30,31]. This can also explain the higher activity of the Fe-Ce-O catalyst since Ceria can have an important role in Fe redox cycle due to the storage oxygen capacity endorsed by this lanthanide. This means that Ce, according to specific needs, may give or withdraw oxygen to Fe, allowing a better electronic equilibrium, which is favourable to oxidation [27]. Table 1 summarizes the catalysts BET surface areas as well as the degree of mineralization attained after 120 min of Fenton's peroxidation. Comparing the commercial catalyst N-150 with the laboratorial Fe-Mn-O 70/30 it seems that the better results regarding TOC removal attained by this catalytic system can be related with the higher BET surface area. In fact, while N-150 shows a $S_{\text{BET}} = 133 \text{ m}^2 \text{ g}^{-1}$ leading to 36% of mineralization, a higher degradation of 45% is attained by Fe-Mn-O 70/30 with $S_{\text{BET}} = 229 \text{ m}^2 \text{ g}^{-1}$. Nevertheless, such relationship is not observed when one compares the latter results with Fe-Ce-O 70/30 which presents a $S_{\text{BET}} = 188 \text{ m}^2 \text{ g}^{-1}$, thus lower than Fe-Mn-O 70/30, showing a higher activity with 57% of TOC depurated after 120 min of reaction. Within these results, it seems that

Table 1
Catalyst BET surface area and TOC removal attained after 120 min.

Catalyst	$S_{\text{BET}} (\text{m}^2 \text{ g}^{-1})$	TOC removed (%)
N-150	133	36
Fe-Mn-O (70/30)	229	45
Fe-O	107	20
Fe-Ce-O (80/20)	191	49
Fe-Ce-O (70/30)	188	57
Fe-Ce-O (50/50)	205	43
Fe-Ce-O (30/70)	115	18
Ce-O	122	22

Table 2

COD, BOD₅ and the ratio BOD₅/COD quantification for the treated wastewater after Fenton's oxidation over the solid catalysts under study.

Catalyst	COD (mg O ₂ L ⁻¹)	BOD ₅ (mg O ₂ L ⁻¹)	BOD ₅ /COD
N-150	850	364	0.43
Fe-Mn-O (70/30)	610	214	0.35
Fe-Ce-O (70/30)	520	485	0.95

the kind of metals presents in the catalyst has more impact over activity than surface area.

Even though the high importance of TPh and TOC removal analysis, these parameters are not considered in current environmental laws, being hence imperative to examine the effluent COD and BOD₅ final values, which are legislated, in order to infer about the possible direct discharge of the treated wastewater into natural water resources. Table 2 resumes these values for each catalytic system under study after 120 min of reaction time. According to European environmental legislation, COD and BOD₅ values below 150 and 40 mg O₂ L⁻¹ are required for safe release of liquid effluents which is clearly not accomplished by the final wastewaters after heterogeneous Fenton's treatment since from the tabulated data, the final values are 850 mg O₂ L⁻¹ (COD) and 364 mg O₂ L⁻¹ (BOD₅) for N-150, 610 mg O₂ L⁻¹ (COD) and 214 mg O₂ L⁻¹ (BOD₅) obtained by the catalytic system involving Fe-Mn-O (70/30) and 520 mg O₂ L⁻¹ (COD) and 485 mg O₂ L⁻¹ (BOD₅) for Fe-Ce-O (70/30). According to the literature, BOD₅/COD ratio allows to infer about the effluents biodegradability and for values higher than 0.4 the residual water is considered as totally biodegradable. Hence, even if 120 min of Fenton's oxidation over the solid catalyst Fe-Ce-O (70/30) was not sufficient to acquire an effluent within the environmental specifications for a secure discharge, the resultant wastewater is highly biodegradable presenting a BOD₅/COD ratio of 0.95 (Table 3) which means that an activated sludge post-treatment should be appropriate to further depuration. The other catalytic oxidation systems are able only to slightly increase the biodegradability relatively to the 0.30 ratio measured for the initial phenolic mixture.

Within these results, the Fe-Ce-O (70/30) catalyst was then selected and the effect of the molar proportion between Fe/Ce was further studied. Fig. 2 represents TPh (a) and TOC (b) abatement along Fenton's using Ce-O, Fe-Ce-O (80/20), Fe-Ce-O (70/30), Fe-Ce-O (50/50), Fe-Ce-O (30/70) and Fe-O. All the catalysts present high activity regarding TPh removal, especially those including Fe/Ce ratios of 80/20 and 70/30 reaching almost 90% and 100% of degradation after 120 min of reaction, respectively. The catalysts with Ce molar quantities higher or equal to Fe (Ce-O, Fe-Ce-O (30/70), Fe-Ce-O (50/50)) revealed lower TPh removals. Ce-O is the less active catalyst with 45% of TPh removed after 120 min, while the oxidation systems involving Fe-Ce-O (30/70) and Fe-Ce-O (50/50) have identical profiles achieving the same final depletion (57%). The iron oxide (Fe-O) shows better results than these catalysts with 70% of TPh abated after 2 h of reaction. However, Ce is yet important for the catalytic activity, since Fe-Ce-O (70/30) and Fe-Ce-O (80/20) are the most efficient, pointing out a synergetic effect between these two

Table 3

COD, BOD₅ and the ratio BOD₅/COD quantification for the treated wastewater after Fenton's oxidation over the tested Fe/Ce catalysts.

Catalyst	COD (mg O ₂ L ⁻¹)	BOD ₅ (mg O ₂ L ⁻¹)	BOD ₅ /COD
Ce-O	840	290	0.34
Fe-Ce-O (80/20)	510	180	0.35
Fe-Ce-O (70/30)	510	485	0.95
Fe-Ce-O (50/50)	600	237	0.39
Fe-Ce-O (30/70)	720	219	0.30
Fe-O	700	289	0.41

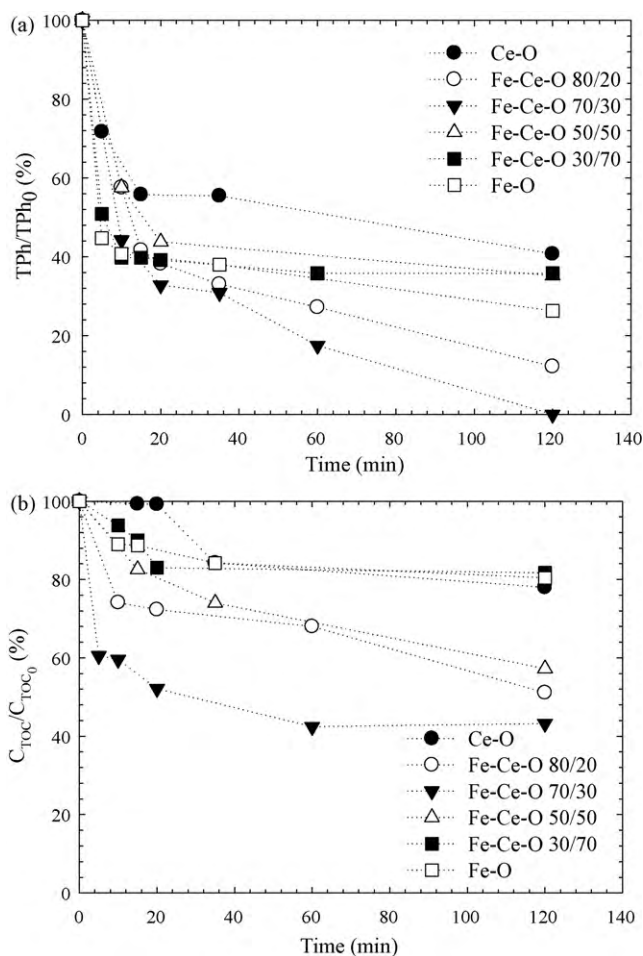


Fig. 2. (a) Effect of the Fe/Ce molar ratio over the heterogenous Fenton's depuration performance concerning TPh and (b) TOC removal. (1.0 g L⁻¹ of catalyst, [H₂O₂] = 244 mM and pH 3.)

elements related with the more efficient electron transfer due to the presence of Ce [27,28]. In what regards the mineralization of simulated effluent, similar results were achieved with both laboratorial catalysts. The catalytic system involving Ce-O is the less efficient with a 20 min induction period in which negligible TOC is removed attaining 20% of degradation after 2 h of reaction time. Despite the same degradation rates are achieved, no induction period is found when Fe-O and Fe-Ce-O 30/70 are applied as the catalytic system. Fe-Ce-O 50/50 and Fe-Ce-O 80/20 show similar depletion profiles with higher reaction rates than the former catalytic systems summing up around 50% of mineralization at the end of the process. Once more, Fe-Ce-O 70/30 is the most promising catalyst with a TOC removal of 57% after 120 min of reaction. Table 1 reveals no evident relationship between Fe/Ce catalysts activity and their BET surface areas. In fact, the best mineralization degree was attained by Fe-Ce-O 70/30 (57%) with a $S_{BET} = 188 \text{ m}^2 \text{ g}^{-1}$, while both Fe-Ce-O 80/20 and Fe-Ce-O 50/50, presenting higher areas (191 and 205 m² g⁻¹, respectively), led to only 49% and 43% of TOC removal after 120 min of reaction. COD, BOD₅ and the biodegradability measured as the ratio between these two parameters (BOD₅/COD) are presented in Table 3 for the final effluent treated during 120 min by heterogeneous Fenton's process using the Fe/Ce catalysts. According to tabulated data, one can observe that none of the treatment systems lead to an effluent disposable in the natural water courses after 120 min of depuration since COD and BOD₅ values are still higher than 150 and 40 mg O₂ L⁻¹, respectively. Nevertheless, the previous most active catalyst regarding the effluents mineralization

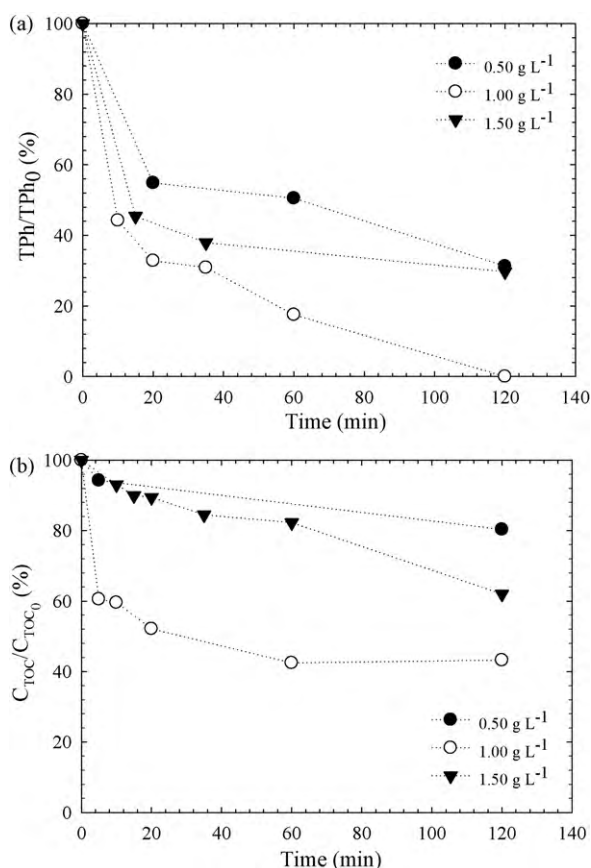


Fig. 3. (a) TPH and (b) TOC degradation along time for several Fe-Ce-O 70/30 catalyst loads. ([H₂O₂] = 244 mM and pH 3.)

(Fe-Ce-O 70/30) also enables the highest biodegradable effluent with a BOD₅/COD ratio of 0.95 in opposition to other catalytic systems that only slightly improved the wastewater biodegradability. These results strongly point out the crucial relevance of undertaking biodegradability analysis whenever a catalyst is meant to be selected for a specific treatment process. Indeed, the chemical COD parameter provided by the solids with 80% and 70% of iron is the same (510 mg O₂ L⁻¹) whereas the biodegradable character of the final effluent treated by Fe-Ce-O 70/30 is almost total (0.95) so that Fe-Ce-O 80/20 is not able to give a readily biodegradable wastewater with BOD₅/COD equal to 0.35 which is even below the threshold commonly accepted of 0.4. Hence, as already pointed out an efficient biological treatment can be implemented after a Fenton's unit with Fe-Ce-O 70/30 concerned to transform initial pollutant into biodegradable species.

3.3. Effect of the catalyst concentration

Increasing the Fe-Ce-O 70/30 catalyst concentration from 0.5 to 1.0 g L⁻¹ the process rate regarding both TPH (Fig. 3(a)) and TOC (Fig. 3(b)) depletion also improved, since a higher number of active sites were available for hydrogen peroxide decomposition into hydroxyl radicals. Nevertheless, when the catalyst is in excess, scavenge reactions can occur between the iron species and the hydroxyl radicals which reduce the system oxidation efficiency (Eqs. (3)–(6)) [12]. In fact, our results show a decrease on both TPH and TOC removal when the catalyst load increases from 1.0 to 1.5 g L⁻¹. Hence, the following experiments were performed using 1.0 g L⁻¹ on Fe-Ce-O 70/30.

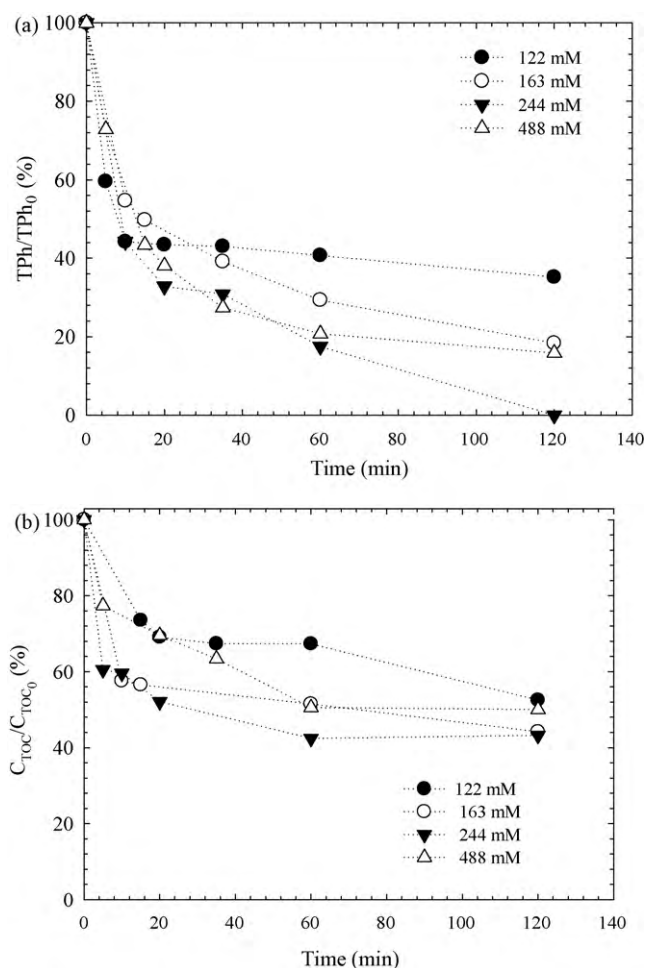
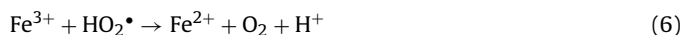


Fig. 4. (a) Effect of hydrogen peroxide concentration over TPH and (b) TOC depuration. (1.0 g L⁻¹ of Fe-Ce-O 70/30 and pH 3.)



3.4. Effect of the hydrogen peroxide concentration

In what concerns the treatment process operational costs, hydrogen peroxide has a high impact. Moreover, above a certain concentration this reactant is well known by the hydroxyl radicals scavenge ability [32] reducing the depuration efficiency (Eq. (7)). Therefore, the hydrogen peroxide concentration effect should be tested in order to maximize the wastewater treatment and reduce operational costs.



Fig. 4 shows the results obtained for TPH (a) and TOC (b) degradation using different H₂O₂ loads in the range of 122–488 mM ranging between two and eight times the stoichiometric value theoretically needed for the total degradation of the initial pollutants (61 mM). The phenolic content removal and the wastewater mineralization increase when the hydrogen peroxide concentration raises from 122 to 244 mM once more hydroxyl radicals are formed. The further augment leads to a decrease on the process efficiency though, since the excess hydrogen peroxide scavenges the hydroxyl radicals (Eq. (7)) and, even if other radicals may be formed (HO₂[•]), their oxidation potential is much lower than the one attributed to HO[•]. TPH

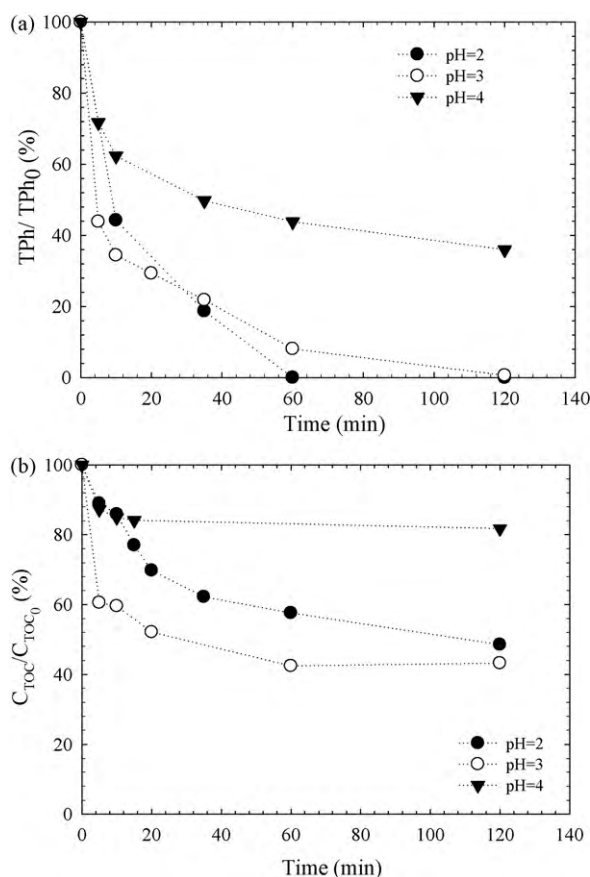


Fig. 5. (a) Normalized TPH and (b) TOC concentration for heterogeneous Fenton's over Fe-Ce-O 70/30 using different medium pH values. (1.0 g L^{-1} of catalyst and $[\text{H}_2\text{O}_2] = 244 \text{ mM}$.)

removal increases from 65% to 100% when $[\text{H}_2\text{O}_2]$ raise from 122 to 244 mM but falls to 84% with the augment to 488 mM on hydrogen peroxide. The effect of the oxidant concentration has less impact over the effluents final mineralization with an increase from 48% to 57% for $[\text{H}_2\text{O}_2] = 122$ and 244 mM, respectively, whereas a decay to 50% is observed for 488 mM. Even though these similar final results, the mineralization rate is higher when 244 mM of hydrogen peroxide are used. Within these results, the subsequent experiments were performed using a hydrogen peroxide concentration of 244 mM.

3.5. Effect of pH

pH is a parameter of major importance on heterogeneous Fenton's process, since it affects the catalyst stability regarding iron leaching and H_2O_2 life-time, which quickly decomposes into oxygen and water at high pH values reducing the treatment capacity. Therefore, the effect of this operational factor was studied in the range of 2–4 and the results concerning TPH and TOC and represented in Fig. 5(a) and (b), respectively. Slower TPH and TOC removal rates are observed for the higher pH value used (pH 4) probably due to the lost of hydrogen peroxide by its decomposition into O_2 and H_2O without the formation of significant quantity of hydroxyl radicals. For these conditions barely 60% of the phenolic content is degraded and only 20% of mineralization occurs after 120 min of reaction. Better results are achieved for pH 3 with TPH totally disappearing and 57% of TOC removed after 2 h of treatment. When pH is set at 2, TPH degradation profile is almost the same that for pH 3, but mineralization is inhibited with a final value of 50%. In fact, pH 3 was already reported as optimal for both homogenous

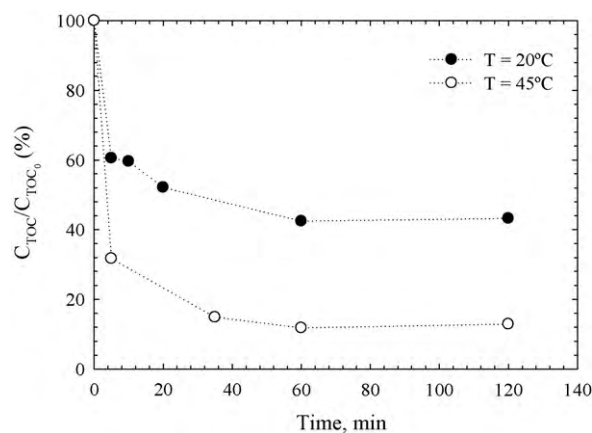


Fig. 6. Temperature effect on TOC removal. (1.0 g L^{-1} of catalyst, $[\text{H}_2\text{O}_2] = 244 \text{ mM}$ and pH 3.)

[33] and heterogeneous Fenton's [9]. From an economical point of view this is an interesting result since the optimal pH is near the one of the original wastewater reducing, therefore, the operational costs associated to pH correction.

3.6. Effect of temperature

Fig. 6 depicts the effect of temperature on heterogeneous Fenton's over Fe-Ce-O 70/30 efficiency regarding mineralization (1.0 g L^{-1} on Fe-Ce-O 70/30, $[\text{H}_2\text{O}_2] = 244 \text{ mM}$ and pH 3). TOC removal profile attained at $T = 20^\circ\text{C}$ (room temperature) is compared with the one obtained when a higher temperature is applied (45°C). As expected by the Arrhenius law, a higher reaction rate is observed for 45°C leading to a final depuration of 87% when compared with the 57% gathered up for 20°C . Ramirez et al. [9] verified that the increase of temperature from 50 to 70°C led to similar final degradations of Orange II which was related with the fact that the increase in temperature also accelerates the decomposition of hydrogen peroxide into useless oxygen and water.

Nonetheless, one of the main advantages of Fenton's process is related with the fact that the reaction can occur at ambient conditions of pressure and temperature contrarily to, for example, wet oxidation requiring the reactor pressurization and heating up. Industrially, this means lower operational costs. Therefore, even though this high improvement attained with the augment of temperature, in the following experiments, regarding the possible integration between this chemical technology and aerobic depuration systems, room temperature was considered.

3.7. Biodegradability and toxicity assessment

The low biodegradability associated to phenolic wastewaters does not allow the direct application of bio-treatments and, on the other hand, chemical treatments are usually expensive. It is then industrially attractive to use an AOP to firstly improve the effluents ability to bioremediation and afterwards implement an inexpensive and effective biological process for final depuration [34]. In this ambit, the evaluation of the heterogeneous Fenton's efficiency may not be only devoted to TOC or COD removal but has to have also into account the resulting effluents biodegradability. Fig. 7 shows COD, BOD₅ and the BOD₅/COD ratio evolution along time when heterogeneous Fenton's used the optimal conditions attained earlier (1.0 g L^{-1} on Fe-Ce-O 70/30, $[\text{H}_2\text{O}_2] = 244 \text{ mM}$ and pH 3). Even if a high depuration efficiency is attributed to this process, after 120 min of reaction, neither COD nor BOD₅ values accomplish the legal threshold (150 and $40 \text{ mg O}_2 \text{ L}^{-1}$, respectively) for the direct discharge of the treated effluent on natural water resources. The

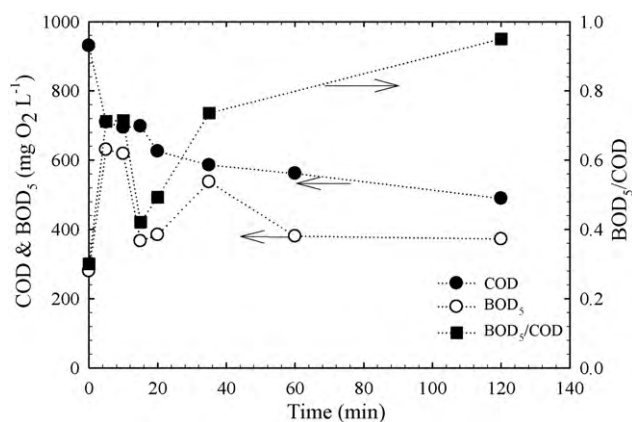


Fig. 7. COD, BOD₅ and BOD₅/COD evolution along the Fenton's treatment time. (1.0 g L⁻¹ of Fe-Ce-O 70/30, [H₂O₂] = 244 mM and pH 3.)

lower COD value obtained is 520 mg O₂ L⁻¹, and BOD₅ increases along the first 20 min, decaying afterwards to 380 mg O₂ L⁻¹ after the 2 h of treatment. The biodegradability results measured as the BOD₅/COD ratios show that the chemical process truly improves the effluent susceptibility to be further depurated by biological means. In fact, this ratio grows from 0.30 to 0.7 in 10 min, and after a decay to 0.40 at 20 min reaches 0.95 at the end of the process. Respirometric techniques were also used to assess biodegradability. Fig. 8 shows the respirometric data for the effluent sample withdrawn after 120 min of the chemical treatment (with the operational conditions referred before). As it can be observed the OUR obtained when Acetic Acid I (used as standard since is considered as totally biodegradable) is fed is similar to the one obtained when the treated wastewater is introduced, revealing the effluents high biodegradability. Moreover, negligible differences between the bacteria OUR with acetic acid before (OUR_{acetic acid1}) and after (OUR_{acetic acid2}) being in contact with the treated wastewater sample were found, hence, the reactional sample had no negative impact over the activated sludges. Table 4 presents the biodegradability and toxicity percentages (determined by Eqs. (1) and (2), respectively) along time and a high toxicity removal is observed and this parameter is reduced from 67% to 0% after 20 min of reaction. Also high biodegradability improvement is reached from 2% to 15% in 20 min being the final value 70% for 2 h. Respirometry only measures the readily biodegradability since the test lasts for about 15 min, and,

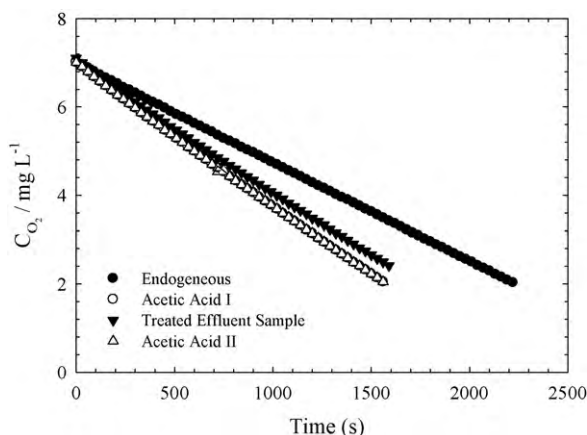


Fig. 8. Respirometric data (dissolved oxygen vs. time) for the phenolic effluent after 120 min of treatment (1.0 g L⁻¹ of Fe-Ce-O 70/30, [H₂O₂] = 244 mM and pH 3). It is also shown the sludge endogenous respiration and respiration at the presence of acetic acid before (Acetic Acid I) and after (Acetic Acid II) the bacteria been in contact with the wastewater sample.

Table 4

Biodegradability and toxicity measured by respirometry along Fenton's peroxidation (1.0 g L⁻¹ on Fe-Ce-O 70/30, [H₂O₂] = 244 mM and pH 3).

Time (min)	Biodegradability (%)	Toxicity (%)
0	2	67
20	15	0
60	51	0
120	70	0

therefore, the values obtained by the BOD₅/COD ratios are higher since BOD is obtained after 5 days [22].

The phenolic compounds are well known by their phytotoxicity and, therefore, by their negative impact over our sensitive ecosystems. Within this context, a depuration treatment should be able to reduce the effluents toxicity in order to safeguard life if the wastewater is discharged into natural stream waters. The toxicity of the original and treated effluent by heterogeneous Fenton's was also evaluated through luminescence techniques using the marine bacteria *V. fischeri*. The effective concentration of effluent (EC) which provokes the light inhibition of 20% and 50% of the microorganisms population (EC₂₀ and EC₅₀) was measured along time and the results are shown in Table 5. As expected, the initial synthetic wastewater presents a high toxicity since the light inhibition of 20% and 50% of the bacteria was attained with a solution containing only 4.5% and 32.2% of the pollutants mixture. During the first 20 min of reaction the effluent's toxicity is not significantly affected by the treatment. Nevertheless, afterwards, a large toxic character reduction occurs with EC₅₀ values out of the scope of the analyzer and EC₂₀ reaching 62.1%. Hence, the heterogeneous Fenton's treatment involving Fe-Ce-O 70/30 is highly effective on the control of the environmental damage towards life species. It is worthy to note that when toxicity is measured by respirometric techniques higher reductions are detected. In fact, while *V. fischeri* bacteria are extremely sensitive, the activated sludge, involving a wide consortium of microorganisms are more resistant and more easily adaptable to chemicals.

3.8. Fresh and used catalyst characterization

The morphology of Fe-Ce-O 70/30, both fresh (Fig. 9(a)) and after 2 h of Fenton's peroxidation (Fig. 9(b)) at the experimental conditions referred before, was observed at different magnifications of SEM (350×, 2000× and 5000×). Even if no significant differences are detected between the two samples it seems that the used catalyst presents a polisher surface. The X-ray diffraction results did not show significant differences between the fresh and used catalyst as well. The amorphous structure of the samples solely allowed identifying Cerium Oxide (Ce₂O₃). The precursors used to produce the catalyst (Fe(NO₃)₃ and Ce(NO₃)₃) encompass Ce and Fe in the trivalent oxidation state. Nevertheless, according to literature [28,35] it is possible that Ce⁴⁺ is also present in the mixed oxide. In fact, Chen et al. [28] refer that, in the case of Mn-Ce-O, the existence of Ce⁴⁺ in a higher concentration than Ce³⁺ promotes the transference of the remaining electrons to Mn facilitating electronic mobility which is favourable to the oxidation reactions. Also, Neri et al. [35] verified

Table 5

EC₂₀ and EC₅₀ evolution along the phenolic mixture treatment by Heterogeneous Fenton's (1.0 g L⁻¹ on Fe-Ce-O 70/30, [H₂O₂] = 244 mM and pH 3).

Time (min)	EC ₂₀ (%)	EC ₅₀ (%)
0	4.5	32.2
20	4.9	29.6
60	12.4	*
120	62.1	*

* The EC value is out of the apparatus scope meaning a high toxicity decrease.

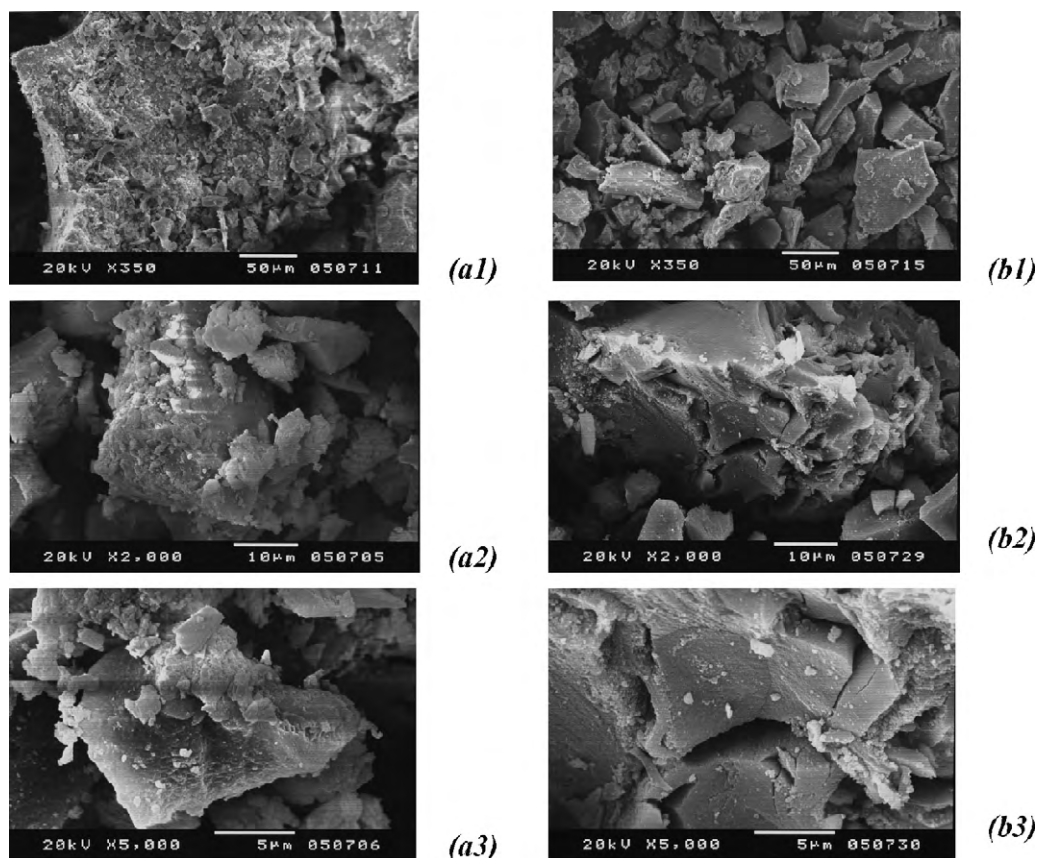


Fig. 9. (a) SEM photographs showing different scales/magnifications of fresh and (b) used Fe-Ce-O 70/30.

a catalytic activity increase when ceria was doped with Fe which was related with the structure modification due to the incorporation of iron ions favouring the oxidation reactions suggesting a strong interaction between Fe^{3+} and Ce^{4+} .

The mercury porosimetry only quantifies pores with diameters higher than 7 nm (for a maximum intrusion pressure of 30,000 psi) and our results showed that neither the fresh nor the used catalyst have macroporous or mesoporous higher than 7 nm. N_2 adsorption revealed a pore size distribution between 2 and 7 nm for both samples with an average value of 6.6 and 6.9 nm for the fresh and used catalyst, pointing out a microporous/mesoporous structure. A slight reduction on the Brunauer–Emmet–Teller surface area (S_{BET}) was observed from 188 to 175 $\text{m}^2 \text{g}^{-1}$. Type IV nitrogen adsorption isotherms at -196°C were found for both fresh and used catalysts. First, the micropores are filled for low relative pressures and then a hysteresis cycle is observed for higher pressures related with the capillary condensation/evaporation in the mesopores.

3.9. Catalyst stability and reuse

The catalyst stability is essential for the industrial application since it has to maintain its activity during long period operation. One of the main drawbacks concerning metallic catalysts is the leaching of the active phase into the liquid and, in this ambit, pH plays an important role [36]. Cerium oxide is reported to be insoluble in water and no important leaching is attributed to this metal [37]. Iron elution was considered and, in order to calculate the percentage of iron leached regarding the Fe initially present in the catalyst, the amount of Fe in the fresh solid was determined to be $530 \text{ mg}_{\text{Fe}}/\text{g}_{\text{Catalyst}}$ by atomic absorption after Fe-Ce-O 70/30 digestion.

Fig. 10 shows the evolution of iron leaching along the experimental time for different pH values (2, 3 and 4). This parameter is clearly affected by pH with higher amounts of the metal dissolved at the lowest pH tested (pH 2) corresponding to 26.8% of the solid initial Fe. The pH increase reduces the iron concentration found in the liquid with 6.8% and 2.3% of the iron initially loaded leached at pH 3 and 4, respectively after 120 min of reaction. To check out the possible intervention of homogeneous catalysis during the treatment process due to the iron leached from the catalyst, three runs were processed at the studied pH values (2, 3 and 4) using $[\text{H}_2\text{O}_2] = 244 \text{ mM}$. $\text{Fe}(\text{SO}_4)$ salt was dissolved in the liquid leading

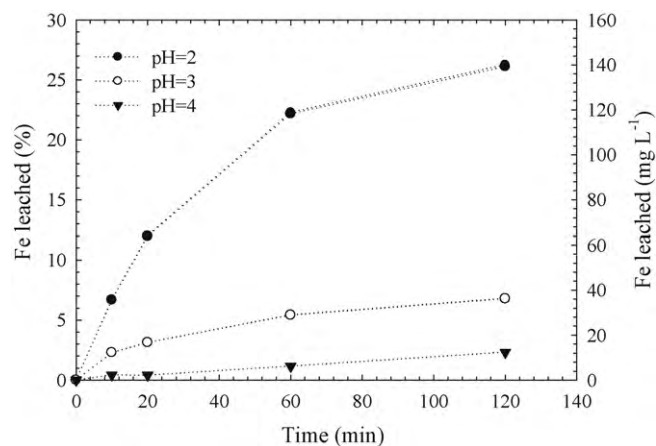


Fig. 10. Iron leached along time as function of the medium pH for Heterogeneous Fenton's process over Fe-Ce-O 70/30. (1.0 gL^{-1} of Fe-Ce-O 70/30 and $[\text{H}_2\text{O}_2] = 244 \text{ mM}$.)

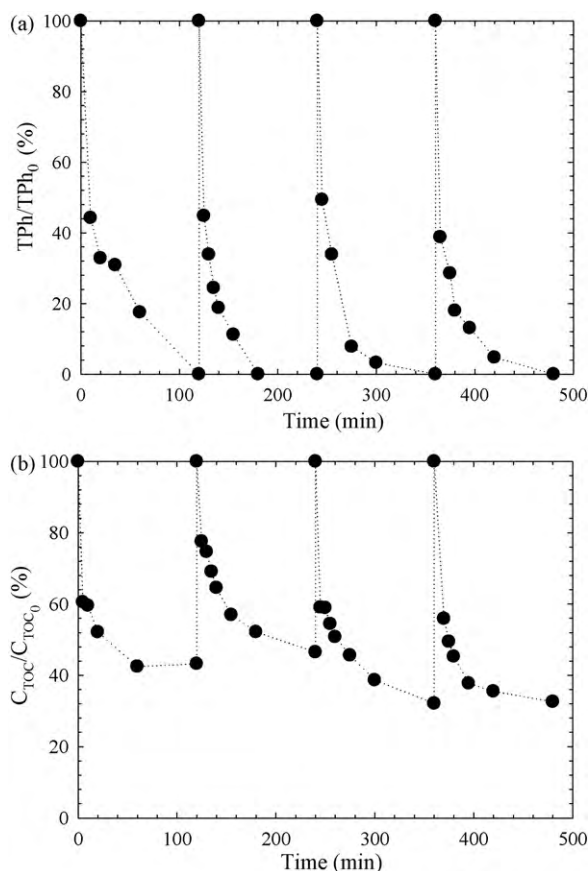


Fig. 11. (a) Normalized TPh and (b) TOC concentration as function of time for a sequential batch experiment with phenolic mixture injection every 120 min.

to a Fe concentration correspondent to the amount leached after 120 min of heterogeneous Fenton's: 140, 37 and 12 mg L⁻¹ for pH 2, 3 and 4, respectively. A final TOC removal after 2 h of reaction of 46% and 7% for pH 2 and 3, respectively reveals that the homogeneous Fenton can have a contribution as high as 89% and 11% on the global mineralization attained by Fenton's peroxidation over Fe-Ce-O 70/30. When pH 4 is considered, the low amount of homogeneous iron led to less than 3% of TOC removed (about 19% of the global mineralization obtained in the heterogeneous process). In this context, even if for pH 2 the importance of the homogeneous catalysis is very high when compared with heterogeneous, for higher pH values a stronger contribution is attributed to the solid Fe-Ce-O 70/30. These data showed the maximum homogeneous contribution once the leached iron from the solid catalyst along the heterogeneous oxidation was lower than the final value, the one used for all the homogeneous experiments.

Also the possible obstruction of the active sites by irreversible adsorption of carbonaceous material at the catalyst surface is an important issue concerning its activity. However, elemental analysis revealed a low carbon amount onto the catalyst at the end (1.0 g L⁻¹ on Fe-Ce-O 70/30, [H₂O₂] = 244 mM and pH 3) corresponding to barely 0.8% of the initial TOC fed to the reactor. Consequently, the effluents depuration is due to the effective oxidation of the pollutants and not to simple adsorption on the solid material.

A first idea about the catalyst performance longer operation times can be given by reusing it in sequential feed-batch trials. Fig. 11(a) and (b) represent TPh and TOC removal during the Fenton's process treatment (1.0 g L⁻¹ on Fe-Ce-O 70/30, [H₂O₂] = 244 mM and pH 3), where fresh effluent was injected every 120 min. For the four reuses performed it seems that the catalytic

activity is not changed for both TPh and TOC maintaining total phenolic depletion and about 57% mineralization after each 2 h of treatment. In fact, a slight improvement on the effluent's depuration seems to occur after the third reuse. Fe-Ce-O 70/30 appears, then, to be an interesting catalyst to be applied on Fenton's process for the depuration of phenolic wastewaters.

4. Conclusions

The heterogeneous Fenton's process was investigated on the depuration of simulated wastewater enclosing six phenolic acids that typically characterize Olive Mill Wastewaters. Firstly, commercial (N-150, Fe-Mn) and laboratory-made catalysts (Fe-Mn-O 70/30 and Fe-Ce-O 70/30) were studied following the catalytic screening methodology based on TPh and TOC removal. Fe/Ce based catalysts have revealed the high removal efficiencies as well as the higher enhancement degree of effluent biodegradability. Subsequently, the molar proportion among the two metals was analyzed giving rise to the synergetic effect between Fe and Ce which delivered to the most active catalyst (Fe-Ce-O 70/30) with total TPh depuration and 57% of TOC removal after 2 h of reaction time. Secondly, main operational parameters were investigated on the effect of process efficiency being observed that an increase in the catalyst concentration from 0.5 to 1.0 g L⁻¹ led to high removals although a further increase to 1.5 g L⁻¹ inhibited the oxidation treatment due to the radical scavenger effect of the iron species in excess. Additionally, the use of hydrogen peroxide concentrations higher than 244 mM affected negatively the Fenton's oxidation process. Therefore, the catalytic screening study led to the selection of the following operating conditions: 1.0 g L⁻¹ of Fe-Ce-O 70/30; [H₂O₂] = 244 mM and pH 3. Even if the use of higher temperature values (45 °C) improved TOC removal, the use of room temperature was preferred since, this way, it will not be required the reactor heating up which reduces the operational costs.

As long as effluent biodegradability and toxicity play a dominant role in the secure and proper disposal of wastewater streams, BOD₅/COD ratio and respirometric methods showed that treated effluent after 120 min reaction time was not still amenable to be directly discharged into the natural water courses so an efficient and inexpensive biological post-treatment is possible to be applied due to the high final biodegradability of the treated stream. Toxicological tests revealed that the ecological impact was reduced during Fenton's process with a high toxicity decrease during oxidation time.

Finally, the Fe-Ce-O 70/30 catalyst exhibited a microporous/mesoporous structure with a *S*_{BET} of 188 m² g⁻¹ and an average pore diameter of 6.6 nm. Moreover, neither significant morphological nor structural differences were found between the fresh and used catalyst. The catalytic stability was also assessed through several feed-batch trials for long time stages and it was found that catalytic activity remained fairly invariable after the recycling process. Within these results Fe-Ce-O 70/30 seems to be quite promising catalytic formulation devoted to the wastewaters remediation by Fenton's process.

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